

Specific heat study of spin-structural change in pyrochlore $\text{Nd}_2\text{Mo}_2\text{O}_7$

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By measurements of specific heat, we have investigated the magnetic field (H) induced spin-structural change in $\text{Nd}_2\text{Mo}_2\text{O}_7$ that shows spin-chirality-related magneto-transport phenomena. A broad peak around 2 K caused by the ordering of 2-in 2-out structure of the Nd moments at zero H shifts to the lower temperature (T) up to around 3 T and then to the higher T above around 3 T with increasing H for all the direction of H . This is due to the crossover from antiferromagnetic to ferromagnetic arrangement between the Nd and Mo moments. While the peak T increases monotonically above 3 T for $H//[100]$, another peak emerges around 0.9 K at 12 T for $H//[111]$, which is ascribed to the ordering of 3-in 1-out structure. For $H//[110]$, a spike like peak is observed at around 3 T, which is caused perhaps by some spin flip transition.

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Novel magnetic phenomena are frequently observed due to geometrical frustration in pyrochlore oxides where the magnetic ions reside on the vertices of linked tetrahedra. One such example is the so-called “spin ice” state in $R_2\text{Ti}_2\text{O}_7$ ($R=\text{Ho}, \text{Dy}$).¹ In $\text{Dy}_2\text{Ti}_2\text{O}_7$, for example, the ferromagnetic interaction among Ising-like Dy moments induces the 2-in 2-out structure, in which the two Dy moments in a tetrahedron point inward and the other two moments point outward. However, there are macroscopically large numbers of spin structures satisfying the 2-in 2-out rule. Consequently, the macroscopically degenerate ground state is realized in this material as shown by Ramirez *et al.*²

In $\text{Nd}_2\text{Mo}_2\text{O}_7$, the Nd moments show the 2-in 2-out structure similarly to the spin ice materials.^{3,4} In this material, however, the spin-polarized itinerant Mo $4d$ electrons coexist with the Nd moments. The Mo and Nd sublattices have the same structure, but are displaced from each other by half a unit cell. Although the anisotropy of the Mo $4d$ moments is small, the Mo moments are slightly (at most by several degrees^{3,4}) tilted from the direction of the net magnetization due to the antiferromagnetic interaction with the Ising-like Nd moments. Recently, an unusual behavior of anomalous Hall effect was observed in $\text{Nd}_2\text{Mo}_2\text{O}_7$ and the origin was proposed to be the spin chirality induced by such a non-coplanar spin structure of Mo moments.³ In this paper, we investigate the spin-structural change in $\text{Nd}_2\text{Mo}_2\text{O}_7$ by means of specific heat measurements. Most of the arguments are concerning the Ising-like Nd moments. We find many behaviors similar to those of the spin ice materials although zero point entropy is not observed in this material. Some of these results provide a supporting evidence of the spin chirality scenario for the unusual anomalous Hall effect.

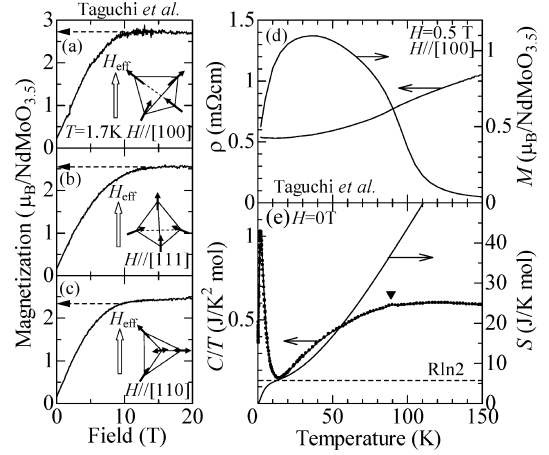


FIG. 1: (a)-(c): Magnetization curves at 1.7 K with magnetic field (H) along (a) [100], (b) [111], and (c) [110] axes. Insets in (a)-(c) show spin structures realized in the high field region of the respective configuration. (d): Temperature (T) dependence of magnetization and resistivity at 0.5 T ($H//[100]$). (e): T -variation of specific heat and entropy at 0 T. Closed triangle indicates the ferromagnetic transition T of Mo spin. The magnetization and resistivity data in (a)-(d) are taken from refs. 3 and 5.

A single crystal of $\text{Nd}_2\text{Mo}_2\text{O}_7$ was grown by floating zone method. The details of the sample growth are reported elsewhere.^{3,5} We reproduce the results of the magnetization and the resistivity for the $\text{Nd}_2\text{Mo}_2\text{O}_7$ crystal at $H=0.5$ T applied parallel to the [100] direction³ in Fig. 1 (d). The resistivity shows a metallic behavior in the whole temperature (T) region ($2 \text{ K} \leq T \leq 150 \text{ K}$). The magnetization begins to increase rapidly with decreasing T below around 100 K, reflecting the ferromagnetic transition of the Mo spin ($T_C \approx 90 \text{ K}$). At around 30 K, the magnetization shows the down-turn due to the ferromagnetic ordering of Nd moments. We reproduce the

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magnetization curves at 1.7 K for the $H// [100]$, $[111]$, and $[110]$ axes in Figs. 1 (a), (b), and (c), respectively.⁵ For all the field directions, enough high- H reverses the Nd moments, resulting in the saturate moments that are much larger than the Mo spin moment ($\approx 1.4 \mu_B/\text{Mo}$). For $H// [100]$ and $[110]$, the saturate moments are in accord with those expected for the 2-in 2-out structure of the Nd moments (see the insets of Figs. 1 (a) and (c)) with the magnitude being $g_{\text{eff}}J \approx 2.3 \mu_B$. These expected values are indicated by the dashed arrows. On the other hand, in the case of $H// [111]$, the saturate moment coincides with that expected for the 3-in 1-out structure (see the inset of Fig. 1(b)), which is also indicated by the dashed arrow. In the canonical case of $\text{Dy}_2\text{Ti}_2\text{O}_7$, the metamagnetic transition from the 2-in 2-out to 3-in 1-out structure is observed as a step-like increase in the magnetization curve for $H// [111]$.^{6,7} However, any trace of such a step is hardly observed in $\text{Nd}_2\text{Mo}_2\text{O}_7$ down to 70 mK.⁵

We measured the specific heat by the conventional relaxation method. The specific heat of $\text{Nd}_2\text{Mo}_2\text{O}_7$ at zero H is shown in Fig. 1(e). A small peak is discerned around 90 K as indicated by the closed triangle. This is owing to the ferromagnetic transition of the Mo spin. In the low- T region (≤ 15 K), the specific heat is dominated by a intense peak, which is caused by the ordering of 2-in 2-out structure in the Nd sub-lattice. These features observed at zero H have already been reported in literature.⁸ We also plot the T -dependence of the entropy S deduced from the T -integration of $C(T)/T$. For the analysis, we assumed the linear relation in C/T below the lowest T (≈ 0.4 K). The S at 15 K is almost in accord with the value of $R \ln 2$, which is expected as from the degree of freedom of Ising moments. Therefore, the entropy of Ising-like Nd moments is mostly released in the low- T (≤ 15 K) region.

In Figs. 2 (a) and (b), we show the T - and H -variation of specific heat of the $\text{Nd}_2\text{Mo}_2\text{O}_7$ crystal below 15 K for $H// [100]$, in which all of the four Nd moments in a tetrahedron make the same angle with the H (see the inset of Fig. 1(a)). Whereas the peak due to the ordering of the 2-in 2-out structure becomes sharper with increasing H below 3 T, it becomes broader and the peak T increases as H is increased from 3 T. We plot the H -variation of the S at 4 K and the peak T in Figs. 2 (c) and (d), respectively. Reflecting the crossover around 3 T in the specific heat, the S at 4 K shows down-turn and the peak T shows up-turn around 3 T. In the canonical case of $\text{Dy}_2\text{Ti}_2\text{O}_7$, the ordering T of 2-in 2-out structure increases with increasing H along the $[100]$ direction.⁹ In the present case, the effective field for the Nd moments that is the sum of the applied H and the *negative* molecular field from Mo spins changes its sign from negative to positive at around 3 T. This is the reason for the non-monotonic H -dependence of S at 4 K and peak T . Therefore, the crossover around 3 T can be ascribed to the reversal of the Nd moments, which is consistent with the results of recent neutron measurements.^{10,11}

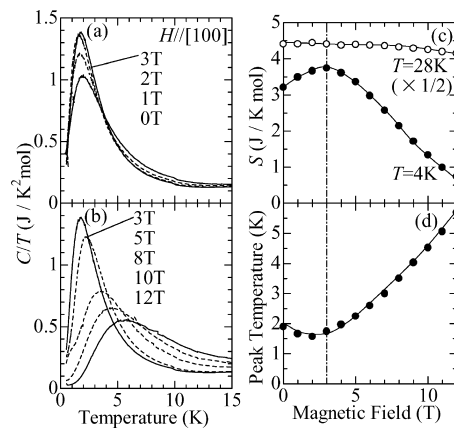


FIG. 2: (a),(b): Temperature (T) and magnetic field (H) variation of specific heat for $H// [100]$. (c): H -dependence of entropy (S) at 4 K and 28 K for $H// [100]$. (d): H -variation of the peak T in the specific heat data shown in (a) and (b). The vertical dot-dashed line in (c) and (d) indicates the crossover H from the antiferromagnetic to ferromagnetic arrangement between Nd and Mo moments. Solid lines in (c) and (d) are merely the guide for the eyes.

We plot the S at 28 K for $H// [100]$ in Fig. 2(c). The entropy originating from the Nd moments is almost completely released below 28 K. Almost H -independent S at 28 K indicates the absence of zero point entropy even at zero effective field for Nd moments, namely at around $H=3$ T, where the decrease of S would otherwise be observed. (The slight decrease of the entropy in the high- H region corresponds to its transfer to the higher- T region above 28 K.) Thus, the ground state degeneracy seems to be lifted by the interaction with the itinerant Mo $4d$ electrons even around 3 T. The S at 28 K shows a similar behavior in the cases of $H// [111]$ and $H// [110]$ (see Fig. 3(d) and Fig. 4(c)), suggesting that zero point entropy has not been observed in any configuration for $\text{Nd}_2\text{Mo}_2\text{O}_7$.

We show the T - and H -variation of specific heat of the $\text{Nd}_2\text{Mo}_2\text{O}_7$ crystal for $H// [111]$ in Figs. 3(a)-(c). In this configuration, one out of four Nd moments in a tetrahedron is parallel to the H as shown in the inset of Fig. 1(b). Similarly to the case of $H// [100]$, the peak due to the ordering of the 2-in 2-out structure becomes sharper with increasing H up to 3 T owing to the decrease of the total effective field. The crossover around 3 T is also discerned in the S at 4 K as shown in Fig. 3(d). Above 3 T, the peak becomes broader with increasing H while the shift of the peak is less significant compared with the case of $H// [100]$. Above around 9 T, the specific heat in the low- T region ($T < 1.3$ K) is gradually enhanced with increasing H . At 11 T, the specific heat shows a much broader peak, which may be viewed as composed of several peaks. Then, at 12 T, another clear peak emerges at low T (≈ 0.9 K). A knee-like structure is also observed around 4 K in the 12 T data. It is worth noting here

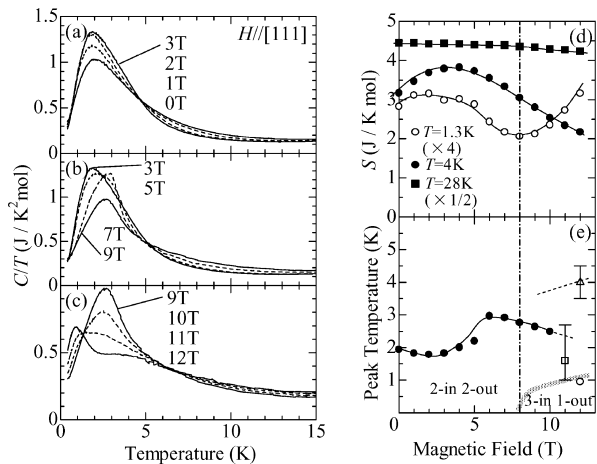


FIG. 3: (a)-(c): Temperature (T) and magnetic field (H) variation of specific heat for $H//[111]$. (d): H -dependence of entropy (S) at 1.3 K, 4 K, and 28 K for $H//[111]$. (e): Characteristic T obtained by the specific heat data for $H//[111]$. Closed and open circles show the peak T due to the ordering of the 2-in 2-out and 3-in 1-out structure, respectively. An open triangle shows the T -position of the knee-like structure in the 12 T data. An open square shows the T -position of the broader peak in the 11 T data. The vertical dot-dashed line in (d) and (e) represents the crossover H at low T from the 2-in 2-out to the 3-in 1-out structure. Solid, dashed, and hatched lines in (d) and (e) are merely the guide for the eyes.

that in $\text{Dy}_2\text{Ti}_2\text{O}_7$ as the reference material, quite a similar peak emerges at low T when the H ($\gtrsim 1$ T) is applied to the [111] direction.⁹ This is ascribed to the ordering of the 3-in 1-out structure (see the inset of Fig. 1(b)). In analogy to this, the low- T peak in the 12 T data for the present compound can also be ascribed to the emergence of the 3-in 1-out structure. This assignment is also supported by the fact that the saturate moment for $H//[111]$ almost coincides with that expected by the 3-in 1-out structure above 12 T. We plot the peak T due to the ordering of the 2-in 2-out structure as with closed circles in Fig. 3(e). An upward shift of the peak T is observed around 3 T similarly to the case of $H//[100]$. The peak T shows a kink at 6 T, above which the peak T slightly decreases with H . We also plot in Fig. 3(e) the T positions of the peak due to the ordering of the 3-in 1-out structure and the knee-like structure in the 12 T data with an open circle and triangle, respectively. The T -position of the broad peak at 11 T is also shown as an open square. The peak due to the ordering of the 3-in 1-out structure exists in the lower- T region compared with that of the 2-in 2-out structure in the lower- H data. The broad specific-heat peak at 11 T ranging over the wide temperature region ($1.0 \text{ K} \leq T \leq 2.7 \text{ K}$), as indicated by the open square with a long vertical bar, can be ascribed to this heavily mixed state of the 2-in 2-out and 3-in 1-out configuration in this T - and H -region.

There are several differences in the specific heat for

$H//[111]$ between the cases of $\text{Nd}_2\text{Mo}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$ while the 3-in 1-out structure is commonly observed in these materials. In the specific heat of $\text{Dy}_2\text{Ti}_2\text{O}_7$, the peak due to the ordering of the Dy moments at the apical position of the tetrahedron (see the inset of Fig. 1(b)) parallel to H emerges in the higher- T region than the ordering T of the 2-in 2-out structure when the H is applied along the [111] direction.⁹ This is because the moments parallel to H are more amenable to the H than the other moments. However, for $\text{Nd}_2\text{Mo}_2\text{O}_7$, no clear peak structure of the specific heat is discerned in the higher T region. Although the specific heat concerning the ordering of the moments parallel to H may be distributed above the peak T of the 2-in 2-out structure in the sufficiently high- H region, the interaction with spin polarized itinerant carriers possibly tends to smear out the high- T peak in the case of $\text{Nd}_2\text{Mo}_2\text{O}_7$. (The kink in the peak T around 6 T in Fig. 3(e) may indicate the onset of the separation of the parallel-moment component from the main peak.) Nevertheless, there is a remnant of such a high- T peak in the specific heat of $\text{Nd}_2\text{Mo}_2\text{O}_7$, such as a knee-like structure at around 4 K at 12 T. Another difference is that the spin structure *gradually* changes from the 2-in 2-out to 3-in 1-out structure for $\text{Nd}_2\text{Mo}_2\text{O}_7$ in contrast to the first order phase transition in $\text{Dy}_2\text{Ti}_2\text{O}_7$. In the specific heat, the low- T component ($T < 1.3 \text{ K}$) gradually increases above around 9 T. These suggest that the correlation of the 3-in 1-out structure evolves even in the lower H region than 12 T. To obtain the onset H of the correlation of the 3-in 1-out structure, we plot the H -dependence of the S at 1.3 K in Fig. 3 (d). The quantity shows a minimum at around $H=8 \text{ T}$, which is thought to be the onset H of the correlation of the 3-in 1-out structure. Recently, Taguchi *et al.* observed the sign change in the Hall resistivity for $H//[111]$ and ascribed it to the reversal of the spin chirality caused by the spin-structural change from the 2-in 2-out to 3-in 1-out structure.⁵ The Hall resistivity crosses zero at around $H=8 \text{ T}$, which coincides with the onset H of the correlation of the 3-in 1-out structure estimated by the present results. This is another evidence supporting the spin chirality scenario for the anomalous Hall effect.

We show the T - and H -variation of the specific heat of the $\text{Nd}_2\text{Mo}_2\text{O}_7$ crystal for $H//[110]$ in Figs. 4(a) and (b). In this configuration, two out of four Nd moments in a tetrahedron are perpendicular to the H (see the inset of Fig. 1(c)). Similarly to the cases of $H//[100]$ and $H//[111]$, the peak around 2 K becomes sharper up to 3 T and then broader above 3 T with increasing H . The H -variation of the peak T and S at 4 K is shown in Figs. 4 (c) and (d), respectively. Corresponding to the crossover around 3 T, the S at 4 K shows the maximum. The peak T shows a local minimum around 3 T and then a kink around 6 T. In $\text{Dy}_2\text{Ti}_2\text{O}_7$, a peak emerges in the higher- T region than the peak T due to the ordering of the 2-in 2-out structure.¹² The higher- T peak is ascribed to the ordering of the half of Dy moments that are not perpendicular to the H . In $\text{Nd}_2\text{Mo}_2\text{O}_7$, by contrast, the higher

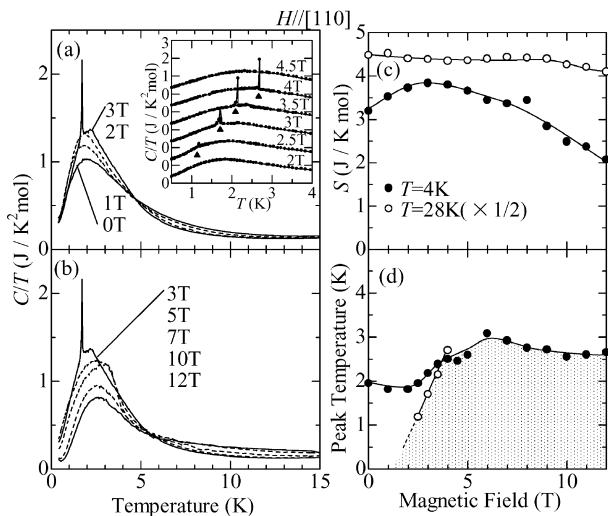


FIG. 4: (a),(b): Temperature (T) and magnetic field (H) variation of specific heat for $H//[110]$. Inset in (a) shows the detailed specific-heat data in the T - and H -region where the spike-like peak is observed. (c): H -dependence of entropy (S) at 4 K and 28 K for $H//[110]$. (d): T -positions of the broad peak around 2 K and the spike-like peak (closed and open circles, respectively). Solid and dashed lines in (c) and (d) are merely the guide for the eyes.

T peak is smeared out possibly due to the interaction with the Mo $4d$ electrons and the kink around 6 T in the peak T may indicate the onset H , above which the half of the moments order ahead of the other two, similarly to the case of $H//[111]$. Because the Nd moments perpendicular to the H are hardly affected by the H , the peak T is kept almost constant in the high- T region above 8 T, which is similar to the $\text{Dy}_2\text{Ti}_2\text{O}_7$ case.¹²

Another distinct feature for $H//[110]$ is the presence of a spike-like peak observed only between 2.5 T and 4.0 T, as exemplified in the inset of Fig. 4(a). The peak becomes sharper and the peak T increases from 1.2 K to 2.7 K with H in this H -region. In Fig. 4 (d), we plot with open circles the T where the spike-like peak emerges. The spike-like peak mainly exists below the peak T due to the ordering of the 2-in 2-out structure. Such a spike-like peak as releasing minimal entropy is expected in the case of a spin-flip transition. Then, the question is what

kind of the spin-flip transition occurs. One possibility is the aforementioned transition from the antiferromagnetic to ferromagnetic arrangement between Nd and Mo moments. As discussed above, the transition exists around 3 T where the spike-like peak is observed. However, the transition is not specific for $H//[110]$. Hence, the spike-like peak should be observed also for the other configurations in this case. Another possibility is the spin-flip transition concerning the Nd moments perpendicular to H . Even if the 2-in 2-out structure is assumed, there are two possible arrangements of the Nd moments perpendicular to H , namely “in-out” and “out-in”, in every tetrahedron for $H//[110]$ (see the inset of Fig. 1(c)). Therefore, there might be the spin-flip transition between nearly degenerate two spin-structural phases where the arrangements of the perpendicular moments are different from each other. However, the recent neutron measurement suggests that the net perpendicular moments does not change up to 5 T.¹⁰ At present, we cannot draw a definite conclusion about the origin of the spin-flip transition. More detailed investigations in terms of diffraction measurements would be needed.

In summary, we have investigated the specific heat in $\text{Nd}_2\text{Mo}_2\text{O}_7$ as functions of direction and magnitude of H as well as T . A broad peak is observed around 2 K at zero H , which is owing to the ordering of the 2-in 2-out structure of the Nd moments. The peak T decreases up to around 3 T and then increases above around 3 T with increasing H irrespective of the direction of H . This is due to the crossover from antiparallel to parallel arrangement between the net magnetizations of the Nd and Mo moments. The peak T increases monotonically above 3 T for $H//[100]$. On the other hand, in the case of $H//[111]$, another peak emerges at around 0.9 K at 12 T, owing to the ordering of 3-in 1-out structure of the Nd moments. This is consistent with the sign reversal of the Hall resistivity reported by a previous study.⁵ For $H//[110]$, a spike-like peak with minimal entropy release is observed at around 3 T, which is ascribed to some spin flip transition.

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